HYDROTREATING AND/OR HYDROCRACKING CATALYST OF HYDROCARBONS AND PREPARATION THEREOF

This invention pertains to a hydroconversion catalyst, the method for preparing it and the use of this catalyst in a hydrotreating and/or hydrocracking process for hydrocarbons, particularly those from petroleum fractions with boiling points preferably between 40 and 560°C.

Currently, the demand for desulfurized, denitrogenized, dearomatized hydrocarbon compounds is increasing and many studies have been conducted in order to develop catalysts that are increasingly effective for purifying hydrocarbons. However, these new catalysts are much more costly and are only accessible to a limited number of producers. In addition, from the first time these catalysts are regenerated, their activity level is much lower than their initial activity level in new condition under the same operative conditions. Only additional specific rejuvenation processing sometimes makes it possible to attain this initial activity level once again and therefore to obtain sulfur contents of less than 10 ppm.

Today, many "traditional" refractory oxide medium-based catalysts containing combinations of metals from groups VIB and VIII are used in refineries in new or regenerated condition either for hydrotreating or for hydrocracking. Although it is impossible to increase their desulfidation and/or denitrogenation activity levels significantly, these catalysts will have to be recovered, stored or destroyed, when the specifications imposed on fuels become so restrictive that it is no longer possible to use them. This storage or this

elimination of solids could also be subject to environmental and safety requirements and could result in significant additional costs for refiners.

The Applicant has therefore endeavored to make refractory oxide-based catalysts that include metals of groups VIB and VIII more effective by modifying them using new methods, in order to give them desulfidation and denitrogenation activity levels that are at least equivalent to those of the best catalysts on the market, and especially superior to their own activity level following regeneration.

All hydrotreating or hydrocracking catalysts are necessarily sulfidized before being used. This sulfidation can be done either *in situ* in the hydrotreatment reactor, or *ex situ* using hydrogen sulfide, mercaptans, sulfides, polysulfides and/or sulfur, in which these compounds are added alone, in a mixture with a solvent or at the same time as the load. Some of these catalysts are modified before sulfidation, and this modification consists of processing these catalysts using chelating, complexing or sulfidizing compounds. It is therefore a well-known process to modify these catalysts using thioglycolic-type acids or even thioalcohols, thioacetone compounds and thiodiazoles, or even thiocyanates, as proposed specifically in the following patents: EP 289211, EP 300629, EP 338788, EP 357295, EP 456592, EP 478365 and EP 506206. Other catalysts have been modified through processing using alcohol-acid organic compounds (EP 482817), mono-, di- or polyalcohols that could potentially be etherified (EP 601722, US 3954673, US 4012340, WO 01/76741), urea-type compounds, polyamines, EDTA, hydrazine and other nitrogen compounds (EP 181035, EP 335754, EP 1043069, WO 01/76741, US 3954673 and US 4012340).

All these modifications are intended to improve the efficacy of catalysts for hydrotreatment, and more specifically for desulfidation. However, these modifications do not always make it possible to obtain the sulfur contents required by the specifications expected to be reached in Europe by 2005 in average distillates from direct distillation or refined fractions, used as components in diesel fuel.

In some countries such as Sweden or the United States, and particularly in California, the total sulfur content of diesel oils is already limited to 0.005% by weight, and this limitation may become the norm eventually in the countries of the OECD. For Europe, this objective of 0.005% by weight of total sulfur must be reached by 2005, but there have already been discussions of 0.001% by 2010.

With this goal in mind, the Applicant has designed a new type of hydrotreatment catalysts with a based of refractory oxides and group VIB and VIII metals from the Periodic Table of the Elements, the performance of which will be improved in terms of desulfidation and/or denitrogenation.

Therefore, the first objective of this invention is a hydrocarbon hydroconversion catalyst, comprising a refractory oxide medium, at least one metal from group VIII and at least one metal from group VIB from the Periodic Table of the Elements, characterized in that in includes an organic compound with at least one oxime group.

The term "oxime group" refers to a group chosen from among the oxime and oxime ether groups according to the IUPAC standard, of the formula:

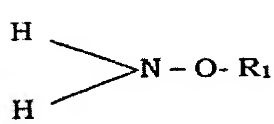
$$> C = NOR_1 \qquad (I)$$

where R_1 is chosen from among hydrogen, the alkyl, allyl, aryl, alkenyl or cycloaliphatic groups and combinations thereof, and these groups can be substituted by at least one electron donor group.

The term "free electron pairs" will be used below to refer to electron pairs that can be at the origin of covalent, dative or coordinative bonds with the transition metals present in the medium.

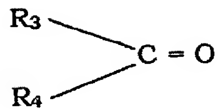
Indeed, the Applicant has established that the presence in the catalyst of an organic compound with at least one oxime group makes it possible, after sulfidation of the catalyst, to attain identical sulfur contents in hydrocarbons with a desulfidation reaction temperature that is at least 5 to 25° C lower, all other operative conditions of the process (pressure, hydrogen quantity and volume velocity per hour (vvh)) being held constant. Such an increase in activity makes it possible to consider obtaining sulfur contents that are well below 50 ppm and even below 10 ppm in treated hydrocarbons, by varying these same operative conditions.

In order to obtain the organic compound described in the invention, it is possible to react an amine of formula (II) below



(II)

in which R_1 is chosen from among hydrogen, the alkyl, allyl, aryl, alkenyl or cycloaliphatic groups, and the combinations thereof, and these groups can be substituted by electron donor groups, with a carbonyl compound of formula (III) below



(III)

in which R_3 and R_4 are chosen (and can either be identical to or different from one another) from among hydrogen for only one of them, the linear, ramified or cyclic hydrocarbon groups of the alkyl, aryl, allyl and alkenyl type, and the combinations thereof, which could potentially be substituted by electron donor groups.

In one preferred method of implementing the invention, the amine of formula (II) is hydroxylamine and the compound of formula (III) is chosen from among the carbonyl compounds of the group formed by ketones and aldehydes.

It would not be outside the scope of the invention to use an organic compound from a synthesis according to the reactions described in the second edition of ORGANIC CHEMISTRY by Francis A. Carey, p. 698 and 712, and in Advanced Organic Chemistry, Reaction, Mechanisms and Structure by Jerry March (third edition).

In the context of this invention, the organic compound comprising this oxime group includes a principal carbonaceous chain consisting of 1 to 40 linear, ramified or partially or completely cyclized carbon atoms, that could potentially be interrupted by sulfur, nitrogen or oxygen heteroatoms or one or more oxime groups, and the carbon atoms can be substituted by hydrogen, by alkyl, aryl, allyl or alkenyl groups and the combinations thereof, by at least one oxime group and/or at least one hydroxyl, sulfidized or polysulfidized group, one thiol, thioacid, thioether or thioester group, one sulfone or sulfoxide group, one amine, amide or imine group, carbonyl, carboxyl, ether or ester groups, ketone or

aldehyde groups, nitric groups, phosphines or any other group with free electron pairs.

In one preferred method of implementing the invention, the organic compound used in the invention includes a single oxime group.

Such a compound with a single oxime group, or monooxime, can be chosen from among the alkyloximes, alkenyloximes, allyloximes, aryloximes and the combinations thereof, alkanoneoximes, cycloalkyloximes, alkanaloximes and benzaldehyde oximes, whether or not they are substituted by alkyl, aryl, arylalkyl or alkylaryl groups.

In a first type of monooxime compound, the organic compound is chosen from the group consisting of 2-octanone oxime, 3-heptanone oxime, tricosanone oxime, heptanone oxime, phenyldodecanone oxime, 1,3-diphenylacetone oxime, benzophenone oxime, 2-phenylcyclohexanone oxime, fluorenone oxime, dimethylbenzaldehyde oxime, benzaldoxime, acetophenone oxime, methylphenanthryl oxime, 2 methylbenzaldehyde oxime, cyclooctanone oxime, 2-phenylcyclohexanone oxime, cyclohexanone oxime, o-ethylhexanone oxime, isobutyraldehyde oxime and acetone oxime.

In a second type of organic compound according to the invention, the organic compound includes one oxime group and at least one second group with free electron pairs.

Although this organic compound includes at least two oxime groups, the organic compound is chosen from among glyoxime, monoalkylglyoximes, dioximes and polyoximes that include alkyl, aryl, alkylaryl and arylalkyl groups. Among these compounds, the dioxime compounds will preferably be chosen from

among glyoxime, monoalkyl and dialkyl oximes with carbonaceous chains with 1 to 10 carbon atoms that tolerate hydrogen and the alkyl, aryl, alkylaryl and arylalkyl groups. The preferred dioxime is dimethylglyoxime.

Although the second group of electron pair donors is not an oxime group, it can be chosen from among hydroxyl, sulfide and polysulfide groups, thiol, thioacid, thioether and thioester groups, sulfone and sulfoxide groups, amine, amide and imine groups, carbonyl, carboxyl, ether and ester groups, ketone and aldehyde groups, nitric groups, phosphines and any other group with free electron pairs.

More specifically, the organic compound is chosen from among mercaptoalkane oximes, alcoxybenzaldehyde oximes, alcoxyarylbenzaldehyde oximes, nitrobenzaldehyde oximes, alcoxybenzaldehyde oximes, hydroxybenzaldehyde oximes, alcoxybenzophenone oximes, substituted carboxaldehyde oximes, nitroarylalcanone oximes, aminobenzaldehyde oximes, benzamide oximes, substituted acetyl oximes, acetyl-furan, -theophene and – pyridine oximes, hydroxyalcanal oximes, amidooximes, acetophenone oximes, hydrazone oximes, polyalcanol oximes, and these groups could potentially be substituted by alkyl, aryl, arylalkyl, alkylaryl, pyridinyl, thiophenyl and furanyl groups, sulfides, alcoxyls, amines, cyanides, nitrates and hydroxyls.

Preferably, the compound will have one oxime group and at least a second group with free electron pairs, which will be chosen from among d-galactose oxime, benzamide oxime, benzyl oxime hydrazone, benzoichydrazide oxime, ethyl-2-oxobutyrate-2-oxime, 2,3 butanedione monooxime, isatine-3-oxime, ethyl(hydro-xyimino)cyanoacetate, di-2-pyridyl-ketone oxime, hydroxypentanal

oxime, 4-pyriylamidooxime, nitrobenzaldehyde oxime, methoxybenzophenone oxime, hydroxybenzaldehyde oxime, dimethylaminobenzaldehyde oxime, 2-acetylpyridine oxime, 4-hexadecyloxybenzaldehyde oxime, methylthioacetaloxime, dimethoxy-nitrobenzaldehyde oxime, methoxyacetophenone oxime, methylbenzamide oxime, thiophenecarboxaldehyde oxime, acetylthiophene oxime, aminobenzo-phenone oxime, acetyl(methyl)thiophene oxime, 2-(4-methoxy-phenyl)glyoxal-1 oxime, 1-mercapto-propoane-2-oxime, aminophenyl-ethane oxime, (octyloxyphenyl)phenyl-methanone, acetylfurane oxime, acetonaphtoquinone oxime, 4-methoxy-3-nitrobenzaldehyde oxime, ethoxybenzaldehyde oxime, methoxybenzaldehyde oxime, 2-(4-methoxyphenyl)glyoxal 1-oxime, 1-mercapto-propan-2-one oxime, 1-(3-nitrophenyl) ethanone oxime, phenanthrene quinine-9-oxime, o-(4-nitrophenyl)acetone oxime, 2(3 or 4) pyridinaldoxime.

Preferably, the catalyst will be a catalyst consisting of a refractory oxide medium, alumina, silica and/or silica-alumina containing 0.1 to 10% of a metal from group VIII by weight, which would preferably be nickel and/or cobalt, and 1 to 20% of a metal from group VIB by weight, and preferably molybdenum.

The catalyst described in the invention preferably contains at least 0.001 mole of the organic compound containing at least one oxime group. More preferably, it contains from 0.001 mole to 10 moles of said compound per mole of metals from groups VIB and VIII.

A second objective of the invention is a process for preparing the hydrotreatment catalyst defined above, characterized in that the organic compound containing at least one oxime group, of commercial origin or obtained by

synthesis, diluted in a solvent, preferably in a hydrocarbon mixture, is put in contact with the catalyst containing a refractory oxide medium, at least one metal from group VIII and at least one metal from group VIB, which is to say, with a traditional commercial catalyst.

In one particular method of implementing the invention, the organic compound containing at least one oxime group is the result of the reaction of a carbonyl compound of formula (III), which may or may not be contained in the hydrocarbons being processed, with an amine of formula (II), by maintaining the mixture at a temperature ranging from room temperature to 100° C, under pressure that is greater than or equal to atmospheric pressure.

In a first variation of the procedure, the organic compound is prepared *in situ* in the hydroconversion reactor, in the hydrocarbons being processed. For example, hydroxylamine is added to a hydrocarbon mixture that naturally contains carbonyl compounds, or in which synthetic carbonyl compounds have been diluted, before putting this mixture in contact with the catalyst.

In a second variation, the organic compound is prepared *ex situ*, which means outside of the hydroconversion reactor, and then is deposited or impregnated on the catalyst, and this deposit or impregnation can take place in the reactor or outside of it.

Of course, any variation of this procedure accessible to an expert in the field also falls within the scope of this invention.

A third objective of the invention is the use of the catalyst described in the invention in a hydrocarbon hydrotreating and/or hydrocracking procedure, after *in situ* or *ex situ* sulfidation of said catalyst using at least one compound chosen from

among hydrogen sulfide, sulfur, CS_2, mercaptans, sulfides and/or polysulfides, and the hydrocarbon fractions, with a boiling point of less than 400° C, contain sulfide compounds or other compounds with a sulfidizing effect, and this compound can be added in the form of a gas or in diluted form in a solvent, or sometimes even as an additive of the load being hydrotreated.

The examples given below in this description are intended to illustrate and not limit the invention.

EXAMPLE 1

In this example, a method of preparing the catalyst according to the invention is described, and this catalyst is then used in the following example.

We begin with a commercial catalyst (catalyst A), consisting of a combination of 3% cobalt by weight and 10% molybdenum be weight in an alumina medium, available on the market and commonly used by refiners in hydrodesulfidation units intended to be impregnated by the "dry" method with dimethylglyoxime (DMG).

The granules of catalyst A are dried at 150° C for four hours in a muffle furnace.

At the same time, in a reactor, a solution in methanol is prepared, containing 50 g/l of DMG. The methanol is heated to 50° C while being stirred continuously. The DMG is then added and the stirring is maintained for a few minutes, until dissolution is complete.

Then, 100 g of dried catalyst A is placed in a 2000-ml Erlenmeyer flask, then 80 ml of the DMG solution in methanol are poured onto the catalyst; the volume of the solution must slightly exceed the porous volume of the catalyst. Finally, the mix thus obtained in the Erlenmeyer flask is stirred vigorously in order to ensure homogenous impregnation of all the granules of catalyst A. The mix is left to rest for maturation for three hours without stirring. Catalyst C_i thus formed *ex situ* is filtered, and then placed in a tube furnace with nitrogen circulation to be dried in said furnace at 80° C for 15 hours.

Once dry, catalysts A and C_i are each loaded into a hydrotreating reactor, then sulfidized by a diesel fuel with a 2%-by-weight dimethyldisulfide (DMDS) additive according to a procedure recommended by the manufacturer of catalyst A.

EXAMPLE II

In this example, the activity levels of catalysts C_i and A are compared to those of commercial catalyst B, after sulfidation, according to the procedure recommended by the manufacturer, which makes it possible to reach post-hydrotreatment sulfur contents of less than 10 ppm.

Catalyst B is a latest-generation Co/Mo catalyst in alumina that is currently the best performing catalyst on the market.

After a catalyst stabilization phase completed by passing it through pure diesel oil, a mix containing 75% diesel by weight and 25% a 220-350° C hydrocarbon fraction by weight that is the result of catalytic cracking, usually

called LCO (Light Cycle Oil), is added. The characteristics of this load are listed in Table I below.

TABLE I

Load Type	25% LCO – 75% GO Mix
Sulfur (ppm)	14447
Density at 15° C (g/ml)	0.8684
Mono-aromatics (% by weight)	18.7
Di-aromatics (% by weight)	14.8
Tri-aromatics (% by weight)	2.8
Aromatics Total (% by weight)	36.3
Nitrogen (ppm)	228
Distillation according to standard ASTM D 86 (°C)	
Initial point	203
5 vol%	230
10 vol%	244
20 vol%	257
30 vol%	268
40 vol%	278
50 vol%	289
60 vol%	301
70 vol%	314
80 vol%	329
90 vol%	347
95 vol%	359
Final point	363

The hydrotreating reaction is performed under pressure of 27×10^5 Pa (27 bars) with a hydrogen/hydrocarbon (H_2/HC) ratio of 130 Nl/l at a volume velocity per hour (vvh) of $1h^{-1}$.

In order to compare the desulfidation and denitrogenation activity levels, the reaction temperature is adjusted to reach either 98% desulfidation or 50% denitrogenation of the load. The higher this temperature, for a given catalyst, and

the lower in comparison to the corresponding temperature for reference catalyst A, the more active this catalyst is in terms of desulfidation or denitrogenation.

For reference catalyst A, the reference temperatures T_{HDS} and T_{HDN}, for hydrodesulfidation and denitrogenation, respectively, correspond to the temperatures required to reach 98% desulfidation and 50% denitrogenation.

Catalyst C_i is prepared as described in Example 1. Catalyst C_i' was prepared according to the *in situ* method in a 100-ml CATATEST pilot, in which a 50-g/l DMG solution was circulated in methanol at a volume velocity per hour of 4 h^{-1}, at atmospheric pressure and at room temperature, and then the entirety was left to mature for two hours.

TABLE II

Catalyst	A	C_i	C_i'	B
HDN	T_{HDN}	- 40° C	- 35° C	- 25° C
HDS	T_{HDS}	- 23° C	- 21° C	- 22° C

As observed, catalysts C_i and C_i' as described in the invention have HDS and HDN activity levels that are significantly higher than those of the traditional catalyst A. Furthermore, compared to the best catalyst on the market, catalysts C_i and C_i' have an HDS activity level that is equivalent to that of commercial catalyst B. Another observation is that C_i and C_i' have an HDN activity level that is significantly greater, which can be a guarantee of the stability of the catalyst over time, as nitrogen is indeed a deactivation factor for hydrotreatment catalysts.